Sulfonation of arylamine Part-5: Preparation and thermal decomposition of di-\(m\)-chloroanilinium sulfate

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White crystalline solid of di-\(m\)-chloroaniline sulfonate (di-\(m\)-CIAS) was obtained when \(m\)-chloroaniline and conc. sulfuric acid were mixed together in the ratio of 1:1 or 2:1 at room temperature. Thermal decomposition of di-\(m\)-CIAS gave two isomeric chloroaminobenzenesulfonic acids (sulfonated products) and kinetics for the same was evaluated using both isothermal and non-isothermal TG data. Di-\(m\)-CIAS seems to decompose by N-H bond heterolysis prior to sulfonation.

Experimental Procedure.

\(m\)-chloroaniline (Johnson purified by distillation) conc. sulfuric acid (AR, Qualigens), silica gel G (TLC grade, Qualigens) and barium chloride (BDH) were used as received.

Preparation and characterization of di-\(m\)-chloroanilinium sulfate (di-\(m\)-CIAS)—White amorphous precipitates of di-\(m\)-CIAS were obtained immediately at room temperature (RT) when \(m\)-chloroaniline mixed with conc. sulfuric acid in 2:1 (\(y = 64\%\)) or 1:1 (\(y = 82\%\)) molar ratio as shown in Scheme 1.

The precipitates were washed repeatedly with \(n\)-butanol, and then recrystallised from mixture of dimethylsulfoxide and dimethylformamide (1:1) in order to remove unreacted \(m\)-chloroaniline and other impurities. White long transparent needle shaped crystals were obtained on keeping the above solution for 48 hrs at room temperature. The purity of the salt was checked by TLC (chloroform: methanol and iodine \(R_f = 0.92\)). The salt was quite stable at room temperature and was found to decompose (\(d 212^\circ \text{C}\)) without melting. It was identified as di-\(m\)-CIAS by elemental gravimetric (sulfur estimation using \(\text{BaCl}_2\)) and spectroscopic analysis. IR spectra were taken on Perkin–Elmer, UV on Hitachi–U–2000 and \(^1\text{H–}\)

![Scheme 1](image-url)
NMR on Varian EM-360, $^{13}$C-NMR on VM-400 and MS on Joel-SX-120 (FAB) spectrometers.

Thermal decomposition studies on di-m-ClAS—Thermal decomposition on di-m-ClAS was studied using the following techniques:

Simultaneous TG-DTG—Simultaneous TG-DTG on di-m-ClAS (wt.10mg, 200-400 mesh) was undertaken at a heating rate of 10°C/min. under a controlled dynamic atmosphere of nitrogen (45 mL/min) on Dupont 990 Modular thermal analysis system in conjunction with 951 thermogravimetric analyser and thermograms are reported in Fig.1.

Non-isothermal TG—TG studies on di-m-ClAS (wt. 10mg, 200-400 mesh) were undertaken in static air at a heating rate of 2°C/min using an indegeneously fabricated apparatus$^{15}$ fitted with temperature indicator cum controller (Model CT 808T Century) and bucket type platinum crucible ($h = 10mm$, dia $= 10mm$). Fraction decomposed ($\alpha$) vs temperature (°C) plot is given in Fig. 2.

Isothermal TG—Isothermal TG on di-m-ClAS (wt. 10mg, 200-400 mesh) was carried out in static air at temperatures 85, 195, 205, 215 and 230°C by indegeneously fabricated TG apparatus and $\alpha$ versus time ($t$) plots are reported in Fig.3a.

DTA—DTA (Perkin Elmer) on di-m-ClAS was carried out in static air using 10mg (200-400 mesh) of sample at a heating rate of 10°C/min. The thermogram (Fig.4) was recorded using a two penpotentiometric strip chart recorder.

Conversion of di-m-ClAS to isomeric chloro-

aminobenzenesulfonic acids (CIABSA)—1.5 g of di-m-ClAS was heated in a tube furnace$^{16}$ at 255±2°C for 1h under reduced pressure (60 mm Hg) and violet coloured mixture was obtained. TLC (chloroform : glc. acetic acid : abs. alc. 4:1:1) of this mixture using iodine showed three spots ($R_f = 0.71$, 0.40 & 0.22). Unsulfonated m-chloroaniline ($R_f = 0.71$) was confirmed by Co-TLC using authentic sample. Doubly distilled water (200ml) and activated charcoal were added to the above heated sample and solution was heated to incipient boiling for 10 minutes. Two compounds (Fractions 1 & 2) were separated out from the solution on cooling the solution to room temperature.

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Fig.1—Simultaneous TG - DTG curve for di-m-ClAS in inert atmosphere

Fig.2—TG curves for di-m-ClAS in static air

Fig.3 (a)—Isothermal TG curve for di-m-ClAS in static air
Results and Discussion

Di-m-CIAS was found to be formed when m-chloroaniline reacted with conc. H$_2$SO$_4$. TG curve reported in Fig.1 showed that di-m-CIAS (I) decomposes in solid state by proton transfer process (Scheme 2) and then thermogravimetric analysis (TGA) and evolved gases analysis. A weight loss of 40.7% (theor. 41.2%) was observed in the temperature range 110-230°C which proves the evolution of water and m-chloroaniline from di-m-CIAS (step 3). It seems that chloroaminobenzenesulfonic acids are formed by C-sulfonation at higher temperatures.

Fraction No. 1 [2-chloro-4-aminobenzenesulfonic acid, 2-Cl-4-NH$_2$C$_6$H$_3$SO$_3$H (IV)]

TLC (R$_f$ = 0.40, chloroform : acetic acid, abs. alc., 1.5 : 0.5 : 0.8) d 310°C, found C 35.16, H 3.18, N 6.6, S 15.41% Cal. for C$_6$H$_6$O$_3$NSCl, C 34.62, H 2.89, N 6.73, S 15.39; UV $\lambda_{max}$ (H$_2$O conc. 0.01%) 332.6 (0.06), 298.4 (1.08), 240.8 (2.62) and 208.8(1.24)nm; MS m/e (relative intensity), 127 (100%), 208 (35.9), 190 (35.8), 137 (30.1), 129 (30.6), 125 (27.3), 100 (17.1), 93 (79.0), 92 (21.0), 90 (19.0), 66 (35.0), 65 (43.0), 63 (28.0), 59 (21.0), 44 (76.0), 42 (14.0); IR(KBr) 1400 - 1410 (vC-Cl), 1160-1190 (vC-Cl), 3340-3450 b, 3040 - 3150 b, 2850 b, 2600 m (vNH), 1550m ($\delta_{NH}$), 1250m (vC-N), 1027-1046 b (vSO$_4$-sym), 1292 (vSO$_4$-asym), 1480s, 882s, 820s (vC=C), 552w, 664w, 718w (vC=C); $^1$H-NMR (DMSO-D$_6$) 6.2-8.1 (pentate 3H) aromatic, 3.8-4.9 (NH$_2$) 137.3, 135.1, 133.9, 129.2, 122.5, 119.9 (6s).

Fraction No. 2 [2-amino-4-chlorobenzenesulfonic acid, 2-NH$_2$-4-Cl C$_6$H$_3$SO$_3$H (V)]

TLC (R$_f$ 0.22, chloroform : glc. acetic acid : abs. alc., 1.5 : 0.5 : 0.8) d 317°C found, C 33.9, H 2.54, N 5.75, S 15.15% Cal. for C$_6$H$_6$O$_3$NSCI, C 34.62, H 2.89, N 6.73, S 15.39; UV $\lambda_{max}$ (H$_2$O conc. 0.01%) 297.6 (0.98), 239.6 (2.5), 216.4 (3.54) nm; MS m/e relative intensity 190 (100%), 210 (33.8), 208 (90.9), 192 (38.1), 173 (24.0), 127 (39.7), 93 (15.1), 44 (18.0); IR(KBr), 1397-1410 (vC-Cl)

<table>
<thead>
<tr>
<th>Fraction No.1</th>
<th>2-Cl-4-NH$_2$C$_6$H$_3$SO$_3$H (IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_f$ = 0.40</td>
<td>Chloroform : acetic acid, abs. alc., 1.5 : 0.5 : 0.8</td>
</tr>
<tr>
<td>d 310°C</td>
<td>Found: C 35.16, H 3.18, N 6.6, S 15.41%</td>
</tr>
<tr>
<td>UV $\lambda_{max}$ (H$_2$O conc. 0.01%)</td>
<td>332.6 (0.06), 298.4 (1.08), 240.8 (2.62), 208.8(1.24)nm</td>
</tr>
<tr>
<td>MS m/e (relative intensity)</td>
<td>127 (100%), 208 (35.9), 190 (35.8), 137 (30.1), 129 (30.6), 125 (27.3), 100 (17.1), 93 (79.0), 92 (21.0), 90 (19.0), 66 (35.0), 65 (43.0), 63 (28.0), 59 (21.0), 44 (76.0), 42 (14.0); IR(KBr)</td>
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<thead>
<tr>
<th>Fraction No.2</th>
<th>2-NH$_2$-4-Cl C$_6$H$_3$SO$_3$H (V)</th>
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<tr>
<td>R$_f$ 0.22</td>
<td>Chloroform : glc. acetic acid : abs. alc., 1.5 : 0.5 : 0.8</td>
</tr>
<tr>
<td>d 317°C</td>
<td>Found: C 33.9, H 2.54, N 5.75, S 15.15%</td>
</tr>
<tr>
<td>UV $\lambda_{max}$ (H$_2$O conc. 0.01%)</td>
<td>297.6 (0.98), 239.6 (2.5), 216.4 (3.54) nm; MS m/e relative intensity 190 (100%), 210 (33.8), 208 (90.9), 192 (38.1), 173 (24.0), 127 (39.7), 93 (15.1), 44 (18.0); IR(KBr), 1397-1410 (vC-Cl)</td>
</tr>
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Table 1---Thermoanalytical data for thermal decomposition of di-m-CIAS

<table>
<thead>
<tr>
<th>TG (wt. loss %)</th>
<th>DTA Endotherm (°C)</th>
<th>DTA DTG Peak temperature (°C)</th>
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<tbody>
<tr>
<td>(Theor) 41.22</td>
<td>(Obs) 40.70</td>
<td>215</td>
</tr>
<tr>
<td>354</td>
<td>356</td>
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</table>
1290, (SO$_4^{2-}$ asym), 1480 s, 820 s (v$_{C-C}$), 715w, 642w, 549 (v$_{C-S}$); $^1$H-NMR (DMSO-D$_6$), 5.7–7.7 (multiplet, 3H aromatic) 3.0–5.0 (–NH$_3$), $^{13}$C(DFCl) $\delta$ = 138.5, 135.0, 1340, 129.2, 122.2, 119.8 (6s).

Cross-sulfonation studies confirmed beyond doubt the occurrence of proton transfer (N–H bond heterolysis$^{17–22}$ in the decomposition of di–m CIAS. Molecular ion peak at m/e 208 also confirms (IV) & (V). Water was confirmed by Karl–Fischer reagent$^{23}$ and m-chloroaniline by chemical and reagent$^{23}$ and m-chloroaniline was found to be superimposable with reported data$^{11,24}$.

A plateau in the temperature range 220 – 290°C (Fig. 1 part B→C) indicates the stability of CIABSA. Further heating (> 300 °C Fig. 1, inert atmosphere) resulted in the decomposition of CIABSA leaving carbonaceous residue (Fig. 1, Part C→D→E). I peak both in DTG (Fig. 1) and DTA (Fig. 4) seems to be due to sulfonation process and II peak due to decomposition of CIABSA.

The kinetics of the thermal decomposition of di–m–CIAS was evaluated by both non–isothermal and isothermal TG data. Non – isothermal TG data was fitted in Mac Callum Tanner equation (MCT)$^{8,25,27}$ (Eq. 1) and values of $E_a$ are reported in Table 2.

$$\ln g(\alpha) = \ln E_a / \phi R - 0.485 E_a (0.435) - 0.449 + 0.217 \times 10^3 \frac{T}{T}$$

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n}$$

where, $g(\alpha) = -\ln(1-\alpha)$.

and $\phi$=heating rate, $E_a$ = activation energy for decomposition and $n$ = order parameter.

The kinetics of the thermal decomposition of di–m–CIAS was also evaluated from isothermal TG data using Parabolic law$^{27–29}$ (Eq. 2) and plots are given in Fig. 3 b.

$$E_a^2 = k t$$

$E_a$ values estimated using MCT & Parabolic law (Table 1) are nearly the same. However $E_a$ for di–m–CIAS has been found less as compared to dianilinium sulfate (28.27 kcal/mol) and di–p–chloroanilinium sulfate (21.25 kcal/mol). This may be due to the strong inductive (–I) effect of m–CI group which may cause weakening of N–H bond and consequently proton transfer is favoured.

<table>
<thead>
<tr>
<th>MacCallum Tanner Eq.</th>
<th>$E_a$ (kcal/mol)</th>
<th>Temp (K)</th>
<th>Parabolic Law</th>
<th>$E_a^2$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order parameter</td>
<td></td>
<td></td>
<td>Rate constant (10$^{-3}$/min)</td>
<td></td>
</tr>
<tr>
<td>n = 0</td>
<td>11.87</td>
<td>458</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>n = 1</td>
<td>11.91</td>
<td>468</td>
<td>1.5</td>
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</tr>
<tr>
<td>n = 1/2</td>
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<td>478</td>
<td>2.5</td>
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</tr>
<tr>
<td>n = 2/3</td>
<td>12.13</td>
<td>488</td>
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<td>503</td>
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<td>11.95</td>
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Conclusions
Solid state decomposition of di-m-CIAS involves proton transfer (unimolecular elementary reaction) process as a primary step and 2-chloro-4-amino-(IV) and 2-amino-4-chlorobenzene-sulfonic acid (V) were found to be the sulfonated products.

Acknowledgments
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References